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BULLETIN
OF THE
CHEMICAL SOCIETY OF JAPAN

VOL. 7

1932

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Published by

The Chemical Society of Japan

c/o Faculty of Science, Imperial University of Tokyo

QD
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OHIO STATE
UNIVERSITY

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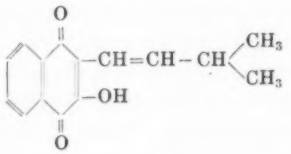
ON THE CHEMICAL CONSTITUTION OF MANGOSTIN. I.

By Seishi YAMASHIRO

Received October 7th, 1931. Published January 28th, 1932.

In the previous studies on mangostin, a yellow colouring matter extracted from the fruit-rind of *Garcinia mangostana*, many molecular formulas and various melting points were given to mangostin. W. Schmid,[1] P.R. Liechti,[2] Nijdam[3] and J. Dekker[4] presented $C_{40}H_{44}O_{10}$ (m.p. 190°C.), $C_{20}H_{22}O_5$ (m.p. 173°C.), $C_{23}H_{24}O_6$ (m.p. 176.5°C.) and $C_{16}H_{16}O_4$ (m.p. 176.5–177°C.) respectively. According to the results of the recent research reported by Dekker (loc. cit.) mangostin has one methoxyl and one hydroxyl groups in a molecule. In support of this fact he has shown that the methoxyl content of mangostin is about 8% (calculated value for $C_{15}H_{13}O_3 \cdot OCH_3$ is 11.4%) and that the methylation of mangostin gives a methylmangostin, which produces an acethyl-methylmangostin on acethylation. He also perceived smells resembling those of amyl alcohol and valerianic acid on alkali-fusion of mangostin, and has come to the conclusion that mangostin may probably be a methoxyl derivative of lapachol which has the annexed formula.



The present author re-examined the experiments carried out by the above mentioned investigators, especially by Dekker, and discovered some other new constituents and properties of mangostin, those of which are intended for a communication. It has, however, to be noted here that the experiments descrived in this paper had been made in 1927, when the publication of them was suspended by some reason, and that they are now communicated without any corrections to the author's opinion of that time, in spite of the fact that striking progress has lately been made in the investigations of mangostin.

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(1) Schmid, *Ann. Chem. Pharm.* **93** (1855), 83.
(2) Liechti, *Arch. Pharm.*, **229** (1891), 426.
(3) *Rec. Trav. Chim. Pays-Bas*, **35** (1916), 346.
(4) Dekker, *Rec. Trav. Chim. Pays-Bas*, **43** (1924), 727.

Mangostin, which the author extracted from the fruit-rind of *Garcinia mangostana* with ethyl alcohol and purified by recrystallisation from benzene and then from dilute ethyl alcohol, is a yellow leaflet crystal, which gives a dark green coloration with ferric chloride in dilute alcoholic solution and melts at 176.5–177°C. The results of the elementary analyses and the molecular weight determinations of mangostin correspond to the formula $C_{20}H_{22}O_5$, but the results of the determinations of methoxyl group give an appreciably lower value (OCH_3=7.50%) than the calculated value (OCH_3= 9.07%) for $C_{19}H_{19}O_4 \cdot OCH_3$.

On methylation with dimethylsulphate and potassium hydroxide in methyl alcoholic solution mangostin gives two kinds of methyl derivatives, both of which are not soluble in dilute alkalies and give the same coloration as that of mangostin with ferric chloride, and also the results of the elementary analyses and the molecular weight determinations of the derivatives correspond almost equally to a monomethyl-mangostin, $C_{19}H_{18}O_3(OCH_3)_2$. But one is a yellowish-white needle crystal (m.p. 120.5–121°C., OCH_3=ca. 14%), which corresponds to the methylmangostin (m.p. 122.5–123°C., OCH_3=ca. 17%) prepared by Dekker, while the other (X) is a pale yellow leaflet crystal (m.p. 171–171.5°C., OCH_3=10.8%). The compound X seems to be an intermediate product of methylmangostin, since the methoxyl content of the former, as will be seen, lies between those of the latter and mangostin and also the compound X converts into the methylmangostin by further methylation with dimethylsulphate and potassium hydroxide.

An acethyl-methylmangostin prepared by acethylation of the methylmangostin with acetic anhydride and sodium acetate crystallises from benzene into white needles (m.p. 191–191.5°C.) and gives no coloration with ferric chloride in alcoholic solution. It corresponds to the acethyl-methylmangostin (m.p. 196°C.) prepared by Dekker, but the results of the analyses and the acethyl determinations correspond to the formula $C_{20}H_{20}O_4(OCH_3)COCH_3$.

Although the acethylation and the benzoylation of mangostin were tried under various conditions and many attempts were made on the separations of reaction products, it was difficult to fractionate the reaction products into pure components. It was, however, accomplished to isolate a compound which corresponds nearly to diacethyl-mangostin.

The methylmangostin seems to be an unsaturated compound, since it easily absorbs bromine in chloroform solution. A brominated methylmangostin prepared by the action of an equimolecular quantity of bromine on the methylmangostin in dry benzene solution is a deep yellow crystalline substance (decomp.p. 160°C.) and has a composition which corresponds almost nearly to a tribromo-methylmangostin. It is, however, so unstable

to water and light that the instability renders the purification of the bromo compound a matter of difficulty, namely, the tribromo-methylmangostin converts instantaneously on contact with water into a reddish-purple viscous matter which on exposure to light passes gradually into a yellow crystalline substance. Consequently it must be recrystallised from dry benzene and kept from moisture and light.

Considering the molecular formula of mangostin as $C_{20}H_{22}O_5 = C_{19}H_{17}O_2(OH)_2\text{-}OCH_3$ from the above experimental results (notwithstanding the low methoxyl content which corresponds rather to $C_{24}H_{26}O_6$ than to $C_{20}H_{22}O_5$), the combined states of two atoms of oxygen are still unknown. To make clear it the author attempted to cause for mangostin the characteristic reactions of flavonol and also to prove the presence of some carbonyl groups in the molecule of mangostin by preparation of oxime and reduced acethylation of mangostin. He failed, however, to give any positive results.

When mangostin is subjected to alkali-fusion many decomposition products are formed. A vapour distilled from the melt during the fusion has an odour resembling that of amyl alcohol, as shown by Dekker, and condences on cooling to a minute quantity of yellow oil. From the melt six compounds can be isolated, of which oxalic, acetic, isovalerianic acids and phloroglucinol have been identified, while the other two compounds remain undetermined. One of the two unknown compounds, however, is a sparingly water-soluble acid which crystallises from water into yellowish-white microscopic needles (m.p. 373°C.) and the other is a water-insoluble yellow phenolic substance (m.p. 212°C.), which bears resemblance to mangostin in its chemical properties, namely, it gives a dark green coloration with ferric chloride and produces on alkali-fusion isovalerianic acid, phloroglucinol, and a vapour resembling amyl alcohol. This phenolic substance, however, differs from mangostin in crystalline form, melting point and composition, having the formula $C_{16}H_{16}O_5$. By the alkali-fusion of mangostin the present author obtained no benzoic acid reported by J. R. Hill[1].

Summary.

Judging from the above experimental results mangostin has the molecular formula $C_{20}H_{22}O_5$ and contains one methoxyl and two hydroxyl groups. It seems to be an unsaturated compound. The formations of isovalerianic acid and the oily matter resembling amyl alcohol by the alkali-fusion of mangostin suggest the presence of a branched side chain in the molecule of mangostin, and the isolation of phloroglucinol from the melt restricts the

(1) Hill, *J. Chem. Soc.*, **107** (1915), 595.

relative positions of methoxyl group, hydroxyl groups and oxygen atoms in the molecule of mangostin.

Although the author has failed to give any positive results in the researches for the characteristic reactions of flavonol and for the presence of carbonyl group in the molecule of mangostin, he has come to the conclusion that the chemical constitution of mangostin as a methoxyl derivative of lapachol is obviously untenable, since it is impossible to yield phloroglucinol from the derivative.

Experimental Part.

Mangostin. The dry powdered fruit-rinds of *Garcinia mangostana* were extracted with alcohol, and from the extracts alcohol was distilled off. The residues were extracted with hot water to remove a reddish-brown viscous matter and after drying were recrystallised from benzene. The yield of the crude mangostin was about 4.3% of the dry rind. The raw product was recrystallised repeatedly from benzene and 60% alcohol. The pure mangostin crystallised from dilute alcohol into yellow plates and melted at 176.5–177°C.

Anal. Subst. = 0.1605 ; CO_2 = 0.4105 ; H_2O = 0.0926 gr. Found : C = 69.75 ; H = 6.46%.

Mol. weight, measured cryoscopically in nitrobenzene, and after Rast. Subst. = 0.0756 ; nitrobenzene = 14.2390 gr. ; f.p. depress. = 0.110°C. Found : mol. weight = 338. Subst. = 0.00135 ; camphor = 0.01168 gr. ; m.p. depress. = 13.5°C. Found : mol. weight = 343.

Methoxyl, measured after Zeizel. Subst. = 0.00412 ; AgI = 0.00251 gr. Found : OCH_3 = 7.50%.

Calc. for $C_{19}H_{19}O_4 \cdot OCH_3$: C = 70.17 ; H = 6.43 ; OCH_3 = 9.07% ; mol. weight = 342, and for $C_{23}H_{23}O_5 \cdot OCH_3$: C = 70.22 ; H = 6.39 ; OCH_3 = 7.55% ; mol. weight = 410.

It was insoluble in water, petroleum ether, carbon tetrachloride and carbon bisulphide, but soluble easily in ether, alcohol, acetone, chloroform, nitrobenzene and acetic acid. It was also soluble in dilute alkalies and gave a dark green coloration with ferric chloride in alcoholic solution.

Methylmangostin. A solution of 10 gr. of mangostin in 300 c.c. of methyl alcohol was shaken with 50 gr. of dimethyl sulphate and then with an excess of 50% potassium hydroxide solution, separating out methylmangostin as a pale yellow crystalline substance. The methylmangostin was filtered after a short standing and washed with water and recrystallised from ethyl alcohol. It crystallised into pale yellow needles from alcohol and melted at 120.5–121°C. The yield was about 7 gr.

Anal. Subst. = 0.1334; CO_2 = 0.3470; H_2O = 0.0831 gr. Found: C = 70.94; H = 6.81%.

Methoxyl, measured after Zeizel. Subst. = 0.00443; AgI = 0.00474 gr. Found: OCH_3 = 14.13%.

Calc. for $C_{19}H_{18}O_3(OCH_3)_2$: C = 70.80; H = 6.74; OCH_3 = 17.42% and for $C_{23}H_{22}O_4(OCH_3)$: C = 70.75; H = 6.60; OCH_3 = 14.60%.

It was insoluble in water and sparingly soluble in cold alcohol, but very soluble in ether, acetone, benzene and ligroine. It gave a dark green coloration with ferric chloride in alcoholic solution.

The methyl alcoholic solution filtered from methylmangostin was evaporated and acidifield with dilute hydrochloric acid, separating out a yellow mass. The separated mass was filtered and recrystallised from ethyl alcohol, crystallising in pale yellow plates which melted at 171–171.5°C. The yield was about 2 gr.

Anal. Subst. = 0.1346; CO_2 = 0.3493; H_2O = 0.0806 gr. Found: C = 70.77; H = 6.70%.

Mol. weight, measured after Rast. Subst. = 0.00088; camphor = 0.00903 gr. m.p. depress. = 11.0. Found: mol. weight = 354

Methoxyl, measured after Zeizel. Subst. = 0.00435; AgI = 0.00358 gr. Found: OCH_3 = 10.86%.

Calc. for $C_{19}H_{18}O_3(OCH_3)_2$: C = 70.80; H = 6.74; OCH_3 = 17.42%; mol. weight = 356.

This compound (X) gave the same coloration as those of methylmangostin and mangostin with ferric chloride, but it was generally less soluble in the ordinary organic solvents than the last two compounds, i.e. sparingly soluble in ether, benzene, chloroform and acetic acid in the cold state. It was also insoluble in dilute alkalies and lowered its melting point exceedingly when mixed with mangostin.

The yield of methylmangostin in proportion to that of the compound X increased with the quantity of dimethyl sulphate employed, and indeed the compound X was converted into methylmangostin on further methylation with dimethyl sulphate and potassium hydroxide.

Acethyl-methylmangostin. Two gr. of methylmangostin was mixed with 4 gr. of anhydrous sodium acetate and 20 gr. of acetic anhydride and heated for 2 hours. On cooling the reaction mixture acethyl-methylmangostin separated out as a white mass, which was filtered and washed with hot water and recrystallised from benzene, yielding white needle crystals; m.p. 191–191.5°C. The yield was about 2 gr.

Anal. Subst. = 0.1371; CO_2 = 0.3512; H_2O = 0.0831 gr. Found: C = 69.86; H = 6.78%. Acethyl. Subst. = 0.5000 gr. equivalent KOH (0.0729N.) = 16.3 c. c. Found: $COCH_3$ = 10.20%. Calc. for $C_{21}H_{22}O_3{\cdot}COCH_3$: C = 69.30; H = 6.60; $COCH_3$ = 10.79%.

It was insoluble in cold dilute alkalies and gave no coloration with ferric chloride in alcoholic solution.

Acethylation and Benzoylation of Mangostin. Four gr. of mangostin was mixed with 20 gr. of anhydrous sodium acetate and 60 c.c. of acetic anhydride and warmed at 40–50°C for 3 days keeping from moisture. The reaction products were extracted with ether and the ethereal solution was shaken with a solution of sodium bicarbonate to remove the acetic anhydride and then the ether was distilled off, leaving a yellow crystalline mass. The yield was about 5 gr. The raw product was fractionally recrystallised from methyl alcohol, yielding two kinds of crystals, namely, plate (m.p. 107–108°C.) and needle (m.p. 115–118°C.) crystals. The latter which was still impure was analysed.

Acethyl. Subst. = 0.5003 gr. equivalent KOH (0.0518 N.) = 41.3 c.c.
Found: $COCH_3 = 18.39\%$. Calc. for $C_{20}H_{20}O_5(COCH_3)$: $COCH_3 = 20.09\%$.

Mangostin was also acethylated with the addition of zinc powder, obtaining none other than the above mentioned reaction products.

Benzoylation was also carried out by the action of benzoyl chloride on mangostin in alkaline solution, but the reaction products were so complex as to render their isolations a matter of difficulty.

Tribromo-methylmangostin. In a solution of 1 gr. of methylmangostin in 10 gr. of dry benzene an equimolecular quantity of bromine was added drop by drop, precipitating a yellow crystalline substance. The precipitates were filtered and recrystallised from dry benzene, forming the aggregates of deep yellow irregular leaflet crystals. The yield was about 1 gr. It decomposed at about 160°C. When this yellow compound had come in contact with water, it converted instantaneously into a reddish-purple viscous matter, which on exposure to light changed gradually again into a yellow crystalline substance.

Anal. Subst. = 0.2041; AgBr = 0.1880 gr. Found: $Br = 39.22\%$. Calc. for $C_{21}H_{23}O_5 \cdot Br_3$: $Br = 40.34\%$.

Alkali-fusion of Mangostin. A mixture of 300 gr. of potassium hydroxide and 50 gr. of water was heated to about 170°C. and 30 gr. of mangostin was gradually added to the fusion mixture under constant stirring. A vapour evolved from the melt during the fusion process was condenced to a yellow oil, which had an odour resembling that of amyl alcohol. When mangostin had been dissolved homogeneously, the melt was cooled and pulverized quickly and dissolved in an ice cold dilute sulphuric acid, leaving a dark brown viscous matter. The aqueous solution was filtered from the

insoluble viscous matter and subjected to steam distillation. Volatile acids were separated from the distillates and fractionated by distillation into two parts. One of the fractions boiled at 117–119°C.; yield ca. 4 gr. It was converted into an anilide by heating with aniline. The anilide melted at 114°C. and was identified with acetanilide. The other fraction boiled at 177–180°C.; yield ca. 4 gr. It was neutralized with ammonium carbonate and heated to 230°C. in a sealed tube, yielding an amide which melted at 135°C. and was identified with isovaleramide.

The aqueous solution from which the volatile acids had been distilled off was extracted with ether. The ethereal solution was washed with a solution of sodium bicarbonate and distilled down to dryness, and the phenolic residue was recrystallised from water, yielding white plate crystals; yield ca. 1.2 gr. It melted at 215°C. in the anhydrous state.

Crystalline water. Air dried subst. = 0.1450; after drying at 120° = 0.1126 gr. Found: H_2O = 22.34%. Calc. for $C_6H_6O_3 \cdot 2H_2O$: H_2O = 22.22%.

Anal. Subst. = 0.1676; CO_2 = 0.3586; H_2O = 0.0747 gr. Found: C = 58.36; H = 5.00%. Calc. for $C_6H_6O_3$: C = 58.43; H = 4.92%.

It produced no precipitates with lead acetate in an aqueous solution and gave bluish-violet coloration with potassium hydroxide and hydrogen peroxide. Phloroglucinol-test with pine tree and concentrated hydrochloric acid was positive and also no depressions in the melting point of the phenolic product were observed when it was mixed with phloroglucinol.

The aqueous solution from which the phenolic part was extracted was concentrated and extracted again with ether, isolating only oxalic acid; yield ca. 1.5 gr.

The dark brown viscous matter separated from the acidic solution of the melt was dried and recrystallised from benzene, forming yellow needle crystals. The yield was about 18 gr. It resembled closely to mangostin in its chemical properties, namely, solubilities in organic solvents, coloration with ferric chloride, and the productions of isovalerianic acid, phloroglucinol, and of a vapour resembling amyl alcohol on alkali-fusion. It, however, melted at 212°C. and lowered its melting point remarkably when mixed with mangostin.

Anal. Subst. = 0.1792; CO_2 = 0.4358; H_2O = 0.0863 gr. Found: C = 66.33; H = 5.40%.

Mol. weight, measured after Rast. Subst. = 0.00056; camphor = 0.00556 gr.; m.p. depress. = 14. Found: mol. weight = 288.

The benzene mother liquor was evaporated and extracted repeatedly with hot water, separating out pale yellow microscopic needle crystals on cooling. It melted at 373°C. The yield was 0.06 gr.

Anal. Subst. = 0.1506 ; CO_2 = 0.3328 ; H_2O = 0.0459 gr. Found : C = 60.27 ; H = 3.41%.

It was insoluble in chloroform and petroleum ether, but very soluble in ethyl alcohol, ether and acetic acid. It was acidic in alcoholic solution and dissolved in dilute alkalies, giving a strong fluorescence.

The last two compounds obtained from the brown viscous matter remain undetermined.

In conclusion, the author wishes to express his hearty thanks to Prof. Riko Majima for his kind guidance in this research.

Chemical Institute, Faculty of Science,
Tohoku Imperial University, Sendai.

A THEORY OF THE RATE OF SOLUTION OF GAS INTO LIQUID.

By Susumu MIYAMOTO.

Received October 1st, 1931. Published January 28th, 1932.

A theory of the rate of solution of gas into liquid, which may be much probable not only for the interpretation of the phenomena already studied by many writers, but also for the interpretation of the rate of oxidation of sodium sulphite solution, was described in the previous papers.[1] The present paper is intended to discuss the new theory in comparison with other theories.

Noyes and Whitney[2] interpreted the rate of reaction at solid-liquid interfaces by the theory based upon the assumptions that the process is composed of two stages, namely extremely rapid reaction in the interfacial layer and slow diffusion of the reactants and resultants from the layer. Nernst[3] extended this diffusion theory and proposed that the reaction velocity in heterogeneous systems is generally composed of two stages above described.

Adeney and Becker[4] had studied the rate of solution of air, oxygen and nitrogen from the surface of bubbles of known magnitude into water, and proposed the following equation to interpret the experimental results,

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(1) S. Miyamoto and T. Kaya, this Bulletin, **5** (1930), 13 ; S. Miyamoto and A. Nakata, ibid., **6** (1931), 18; S. Miyamoto, T. Kaya and A. Nakata, ibid., **6** (1931), 140.
(2) *Z. physik. Chem.*, **23** (1897), 689.
(3) Ibid., **47** (1904), 52.
(4) *Phil. Mag.*, **38** (1919), 317; **39** (1920), 385; **42** (1921), 87.

$$\frac{dw}{dt} = SAp - f\frac{S}{v}w \ , \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where A is the initial rate of solution per unit area, f the coefficient of escape from the liquid per unit area and volume, S the area of the boundary surface, v the liquid volume, p the gas pressure and w the weight of gas dissolved.

Donnan and Masson[1] modified the equation of Adeney and Becker, and proposed the following equations.

$$\frac{dw}{dt} = k_2(kc_g - c_l) \ , \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

when the system obeys Henry's law, and

$$\frac{dw}{dt} = k_2[f(c_g) - c_l] \ , \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2')$$

when Henry's law does not hold.

In these equations, c_g is the concentration of absorbable gas in the gas phase, c_l the corresponding concentration in the liquid phase, k the Henry's law coefficient, and k_2 a constant. The above mentioned equations may be expressed by a slight rearrangement in the form,

$$\frac{dw}{dt} = k[c_\infty - c_l] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where c_∞ is the concentration of saturated solution, and k a constant.

For the rate of solution of gas into liquid, the following expression was proposed by Lewis, Whitman and Keats,[2]

$$\frac{dw}{dt} = k_p[p_g - p_l] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where p_g and p_l are the partial pressure of the absorbable component in the gas phase and in the liquid phase respectively.

Whitman and Keats[3] assumed the existence of a stationary gas film and a stationary liquid film at the boundary surface and proposed the following equation for the rate of absorption.

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(1) *J. Soc. Chem. Ind.*, **39** (1920), 236.
(2) Lewis, *J. Ind. Eng. Chem.*, **8** (1916), 825; Whitman and Keats, ibid., **14** (1922), 185.
(3) Ibid.

$$\frac{dw}{dt} = k_p(p_1-p_2) = k_c(c_2-c_3) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where p_1-p_2 is a partial pressure gradient of the solute in the gas film, and c_2-c_3 is a concentration gradient in the liquid film, k_p and k_c being constants.

Davis and Crandall[1] assumed that the upper surface of the liquid film is almost instantaneously saturated with the gas and interpreted the results of their research on the rate of solution of oxygen into water by the equation,

$$\frac{1}{S}\left(\frac{dn}{dt}\right) = k_l(c_\infty-c_l) \ , \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where c_∞ is the saturation concentration of the dissolved gas, c_l the concentration of the gas in the liquid phase, k_l a constant, n the number of moles of the gas in the liquid phase, and S the area of the boundary surface.

The idea of Davis and Crandall is similar to that of Nernst, Noyes and Whitney, and the equation (6) is quite the same as the equation (3). When the gas reacts with a component in the liquid phase, the rate of absorption of the gas would depend upon the concentration of the solute. Davis and Crandall[2] proposed the following equation for the rate of solution when the reaction velocity is very great,

$$\frac{1}{S}\left(\frac{dn}{dt}\right)_{\text{initial}} = k_l(c_\infty+c_m) \ , \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6')$$

where c_m is the concentration of the reacting solute in the main body.

A New Theory of the Rate of Solution of Gas into Liquid.

The above mentioned theories are based upon two assumptions; the existence of a stationary film of liquid or stationary films of liquid and gas, and the instantaneous saturation of the upper layer of the stationary film with the gas. These assumptions will not be satisfied in some cases, as will be discussed in the later. The existence of stationary film of such thickness as the diffusion theory requires will be questionable, when the bulk of the liquid is well agitated with a proper stirrer, and the assumption of instantaneous saturation of the upper layer of the liquid with gas can not be adopted to interpret the rate of oxidation of sodium sulphite solution.

The theory of the present writer[3] is based upon quite different assumptions, as will be described in the following.

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(1) *J. Am. Chem. Soc.*, **52** (1930), 3757.
(2) Ibid., **52** (1930), 3769,
(3) The theory, described in the previous papers, loc. cit., was slightly revised.

The process of solution of gas into liquid can be separated in two processes, namely the penetration of gas molecules into the liquid phase, and the escape of the gas molecules from the liquid phase. Then the rate of solution of gas into liquid can generally be expressed by

$$\frac{N}{S}\frac{dn}{dt} = N''-N''', \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

where n is the number of moles of the absorbable gas, N Avogadro's constant, N'' the number of molecules of gas which enters into the liquid phase per unit area of the interface per unit of time, N''' the number of molecules of the gas which escapes the liquid phase per unit area per unit of time, and S the area of the boundary surface.

According to the kinetic theory of gases, the value N'' should be a fraction of the number of molecules which collide with the unit area of the interface per unit of time, N', then,

$$N'' = \beta N', \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

where β represents the ratio of the number of molecules which penetrate into the liquid phase and the number of molecules which collide with the liquid phase, N' being the number of molecules which collide with the unit area of the boundary surface per unit of time.

By Maxwell's distribution law of velocities,

$$dN = \frac{N}{\sqrt{\pi}a} e^{-\frac{u^2}{a^2}} du, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

where dN means the number of molecules whose components of velocities at right angles to one definite plane lies between u and $u+du$ among N molecules, and

$$a^2 = \frac{2RT}{M}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

where R the gas constant T the absolute temperature, and M the molar weight of the gas. It is then easily be seen that the value N' can be expressed by

$$N' = \int_0^\infty \frac{N}{V\sqrt{\pi}a} u\epsilon^{-\frac{u^2}{a^2}} du = \frac{Np}{\sqrt{2\pi MRT}}, \quad \ldots\ldots\ldots\ldots \quad (11)$$

Where V is the molar volume of the gas, N Avogadro's constant, P the partial pressure of the gas, N/V being the number of molecules per unit volume of gas.

Now an assumption is proposed. Among the molecules, which collide with the liquid surface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_0, are able to enter into the liquid phase. Then value N'' will be expressed by

$$N'' = \int_{u_0}^{\infty} \frac{N}{V\sqrt{\pi}\alpha} u e^{-\frac{u^2}{\alpha^2}} du = \frac{Np}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \quad \cdots\cdots\cdots (12)$$

From (8), (11) and (12) it is seen that

$$\beta = e^{-\frac{Mu_0^2}{2RT}} \quad \cdots\cdots\cdots (13)$$

From the similar assumption, that among the molecules of gas in the liquid phase, only those, which collide with the interface with the velocities whose components at right angles to the boundary surface are greater than a threshold value u_0', are able to escape the liquid phase, we can obtain the value N''' from the Maxwell's distribution law,

$$N''' = \int_{u_0'}^{\infty} \frac{c_l N}{1000} \frac{1}{\sqrt{\pi}\alpha} u e^{-\frac{u^2}{\alpha^2}} du = \frac{c_l N}{1000} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0'^2}{2RT}}, \quad \cdots\cdots (14)$$

where c_l is the concentration of the gas in the liquid phase, N Avogadro's constant, $c_l N/1000$ being the number of molecules of the gas per unit volume of the liquid. The concentration of the gas in the liquid phase will depend upon the depth of the liquid, and strictly speaking, the mean value of the concentrations of the effective region should be employed for the value c_l, but when the bulk of the liquid is stirred, its concentration may be employed as a first approximation.

From the equations (7), (12) and (14) we have

$$\frac{N}{S}\frac{dn}{dt} = \frac{Np}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} - \frac{c_l N}{1000} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0'^2}{2RT}},$$

or

$$\frac{dn}{dt} = \frac{p}{\sqrt{2\pi MRT}} S e^{-\frac{Mu_0^2}{2RT}} - \frac{c_l}{1000} S \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0'^2}{2RT}}, \quad \cdots\cdots (15)$$

This is the general equation for the rate of solution of gas into liquid, obtained from the new theory. The values of u_0 and u_0' depend upon the nature of gas and liquid.

The initial rate of solution, or the rate of solution of gas when the liquid is perfectly free from the gas, can be obtained from the above equation by putting $c_l = 0$,

$$\left(\frac{dn}{dt}\right)_{\text{initial}} = \frac{p}{\sqrt{2\pi MRT}} S \cdot e^{-\frac{Mu_0^2}{2RT}}, \quad \ldots\ldots\ldots\ldots \quad (16)$$

When the liquid is saturated with the gas, $dn/dt = 0$. Then at the state of saturation,

$$\frac{p}{\sqrt{2\pi MRT}} S e^{-\frac{Mu_0^2}{2RT}} = \frac{c_\infty}{1000} S \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0'^2}{2RT}}, \quad \ldots\ldots\ldots \quad (17)$$

where c_∞ is the concentration of the saturated solution.

Then the equation (15) can be expressed in the form

$$\frac{dn}{dt} = KS(C_\infty - C_l), \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (18)$$

where

$$K = \frac{1}{1000} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0'^2}{2RT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (19)$$

The equation (18) is quite the same as the equation (3). Thus the equation (3), experimentally obtained and theoretically explained by old theories, was also derived from the new theory.

The equations (15), (16) and (18) were derived without the assumption of the existence of stationary boundary films, and these equations will also be satisfied, when the bulk of the liquid phase is quiescent and the existence of a stationary liquid film should be taken into considerations. In this case,

$$n = n_1 + n_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (20)$$

where n is the total number of moles of the absorbed gas in the liquid phase, and n_1 and n_2 the number of moles of the gas in the stationary liquid film and in the bulk of liquid respectively.

$$\frac{dn}{dt} = \frac{dn_1}{dt} + \frac{dn_2}{dt} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (21)$$

Now,

$$\frac{N}{S}\frac{dn_1}{dt} = xN'' - yN''' - K(c_s - c_l) \quad \ldots\ldots\ldots\ldots \quad (22)$$

where xN'' is a portion of gas molecules which enter into liquid phase per unit of area per unit of time, yN''' a portion of gas molecules which escape

the liquid phase per unit of area per unit of time, $K(c_s-c_l)$ the number of molecules of gas which enter into the bulk of liquid from the stationary film by diffusion, c_s the concentration of gas at the upper surface of the film, c_l the concentration in the bulk of liquid, N Avogadro's constant, S the area of the boundary surface, and x and y the constants less than 1.

$$\frac{N}{S}\frac{dn_2}{dt} = (1-x)N''-(1-y)N'''+KS(c_s-c_l). \quad \ldots\ldots\ldots \quad (23)$$

From the equations (21), (22) and (23),

$$\frac{N}{S}\frac{dn}{dt} = N''-N''' \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (24)$$

From the equations (12), (14) and (24) we have

$$\frac{dn}{dt} = \frac{p}{\sqrt{2\pi MRT}}Se^{-\frac{Mu_0^2}{2RT}}-\frac{cS}{1000}\sqrt{\frac{RT}{2\pi M}}e^{-\frac{Mu_0'^2}{2RT}},$$

which is the equation (15), and by a slight rearrangement,

$$\frac{dn}{dt} = KS(c_\infty-c),$$

which is the equations (18). In this case the mean value of concentrations of the effective region should be employed for the value c.

Discussion.

The rate of oxidation of sodium sulphite solution and the effect of many substances on the velocity were investigated by many writers.[1] The present writer has also studied the rate of oxidation of the same substance under special conditions, and from the following reason an assumption, that the rate of oxidation obtained by the present writer is equivalent to the rate of solution of oxygen into water, free from oxygen, was proposed.

(1) The rate of oxidation of sodium sulphite solution, obtained, is the maximum value, which does not increase further with the increase of concentration of sodium sulphite. It was also found that this maximum value is not a specific value of sodium sulphite solution. The maximum velocities

(1) Bigelow, *Z. physik. Chem.*, **26** (1898), 493; Titoff, *Z. physik. Chem.*, **45** (1903), 641; Bäckstrom, *J. Am. Chem. Soc.*, **49** (1927), 1465; Alyea and Bäckstrom, *J. Am. Chem. Soc.*, **51** (1929), 90.

of oxidation of sodium sulphite, stannous hydroxide and ferrous hydroxide are identical under the same conditions.[1]

(2) The rate of oxidation of sodium sulphite solution does not increase above this maximum value with the further increase of concentration of sodium sulphite, on the contrary it decreases when the concentration is very great.[2] The total quantity of these substances oxidized during a definite time interval in a same vessel is not greater than that when they are oxidized alone. The rate of absorption of oxygen by the solution does not increase by mixing them.[3]

(3) The maximum rate of oxidation of sodium sulphite solution is proportional to the area of the interface of the solution.[4] It was also confirmed that this maximum value is proportional to the partial pressure of oxygen.[5]

(4) As was described in the previous paper,[6] the rate of solution of oxygen, calculated from the maximum rate of oxidation of sodium sulphite solution, has nearly the same value as the initial rate of solution of oxygen into water, observed directly by several writers.

From these reasons, the maximum rate of oxidation of sodium sulphite solution is equivalent to the rate of solution of oxygen into water, free from oxygen, which is expressed by the equation (16), according to the theory of the present writer. From the equation (16), the value u_0 was calculated,[7] using the maximum rate of oxidation of sodium sulphite solution, observed, and was found that the value u_0 is 1.65×10^5 cm./sec., approximately 3.4 times the root-mean-square velocity of oxygen gas and is independent of temperature in the range 15°—35°C.

The diffusion theory assumes the existence of a stationary film at the interface. According to the new theory the equation (3) was obtained when the stationary film is not exist, as when the stationary film exists. When the liquid phase is quiescent, the existence of a stationary liquid film will be very probable, but when the liquid phase is well stirred, the assumption that a stationary liquid film of such thickness as that, calculated by Brunner[8] and Crandall[9] from the diffusion theory (2×10^{-2}—2×10^{-3} cm.), exists at the interface, can not be accepted without direct confirmations.

(1) Miyamoto, this Bulletin, **2** (1927), 74; **2** (1927), 155; **3** (1928), 98; **3** (1928), 137.
(2) Miyamoto and Kaya, ibid., **6** (1931).
(3) Miyamoto, this Bulletin, **2** (1927), 192; **4** (1959), 132.
(4) Miyamoto and Nakata, ibid., **6** (1931), 9.
(5) Miyamoto, Kaya and Nakata, ibid., **5** (1930), 229.
(6) Miyamoto and Nakata, ibid., **6** (1931), 22.
(7) Ibid.
(8) *Z. physik. Chem.*, **47** (1904), 99.
(9) *J. Am. Chem. Soc.*, **52** (1930), 3760.

As a result of the study on the oxidation velocity of sodium sulphite solution by oxygen in the presence of molecular film of fatty acid,[1] it was ascertained that when the bulk of sodium sulphite solution is well agitated, the thickness of stationary film, if it exist, should be less than the length of a molecule of palmitic acid (23.7×10^{-8} cm.).

The result of the measurement of the oxidation velocity of sodium sulphite solution studied by the present writer, will be difficult to be interpreted by the diffusion theory, which requires the existence of a stationary film whose thickness is about 10^4 times the value confirmed experimentally[1]. The fact that the rate of oxidation of sodium sulphite solution is independent of the concentration of sodium sulphite in the range of about 0.3—0.7 normal, will also be difficult to be explained by the diffusion theory, according to which the interface is instantaneously saturated with gas. The equation (6′)

$$\frac{1}{S}\left(\frac{dn}{dt}\right)_{\text{initial}} = k_l(c_\infty + c_m) ,$$

which is based upon the assumption that the upper layer of the surface film is almost instantaneously saturated with gas, does not hold in the case of the oxidation of sodium sulphite solution. The oxidation velocity is independent of the concentration in the range above described; it depends upon the concentration when the concentration is very small. According to the theory of the present writer, the rate of oxidation of sodium sulphite solution is less than the initial rate of solution of oxygen into water, when the concentration of sodium sulphite is very small, and the rate of oxidation is greater than the initial rate of solution of oxygen into water, when the concentration of sodium sulphite solution is in the range of 0.3—0.7 normal. In the former case, the rate of oxidation depends upon the concentration of sodium sulphite solution, and in the latter case, the rate of oxidation is equivalent to the initial rate of solution of oxygen into water, free from oxygen, which is expressed by the equation (16), and is independent of the concentration of sodium sulphite solution.

The rate of solution of oxygen into sodium sulphite solution decreases when the concentration of sodium sulphite solution is very great,[2] as was above described. This fact will be explained by the equation (6′), which is based upon the diffusion theory, if the decrease of solubility of gas c_∞ be taken into consideration, but the diffusion theory is not satisfied for the interpretation of the initial stage of the rate of oxidation of sodium sulphite solution, as was above described. According to the new theory it is easily

(1) Miyamoto, Kaya and Nakata, this Bulletin, **6** (1931), 133.
(2) Miyamoto and Kaya, this Bulletin, **6** (1931).

explained by the consideration that in this stage the rate of oxidation is also equivalent to the rate of solution of oxygen into the solution, free from oxygen, which is expressed by the equation (16), but the value u_0, which depends upon the nature of the liquid phase, increases with the increase of the concentration of sodium sulphite solution.

The coincidence of the oxidation velocities[1] of sodium sulphite, stannous hydroxide and ferrous hydroxide in sodium hydroxide solution under the same conditions by air is also a favourable experimental fact to the theory of the present writer. The maximum oxidation velocity of sodium sulphite solution is proportional to the partial pressure of oxygen, as the new theory requires. The maximum oxidation velocity is equivalent to the value expressed by the equation (16).

In conclusion it can be described that the new theory interprets not only the experimental facts which are explained by the diffusion theory, but also those, which will be difficult to be explained by the old theory.

The new theory is very reasonable in the point of view that it does not assume the existence of a stationary liquid film at the interface, since the existence of a stationary liquid film of such thickness as that calculated by the diffusion theory is questionable, when the bulk of the liquid is well agitated with a stirrer.

Summary.

(1) A theory of the rate of solution of gas into liquid was proposed, which is based upon the assumptions that among the molecules of gas, which collide with the interface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_0, can enter into the liquid phase, and that among the molecules of gas in the liquid phase, only those which collide with the interface with velocities, whose components at right angles to the interface are greater than a threshold value u_0', can escape the liquid phase.

(2) A short discussion of the theory in comparison with the old theories was described.

(3) Rate of oxidation of sodium sulphite solution, which will be difficult to be explained by the old theory, was interpreted by the new theory.

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(1) Loc. cit.

THE RELATION BETWEEN KOLBE'S REACTION AND HYDROGEN ION CONCENTRATION. THE MECHANISM OF KOLBE'S REACTION.

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Received October 24th, 1931. Published January 28th, 1932.

Various theories have been advanced to explain the mechanism of Kolbe's reaction, since the great Leipzigian professor discovered it in 1849. None of these theories, however, is convincing for lack of sufficient evidence. The present author has been studying the electrolyses of ammonium and potassium acetates in aqueous solution for some time. The results of his investigation have been published in the Journals of the Chemical Society of Japan in the vernacular language (**51** (1930), 126; **51** (1930), 632; **52** (1931), 249; **52** (1931), 756).

During the author's examination of acetate solutions of smaller concentration, his notice was drawn to the fact that the colours of the indicator added to the electrolyte for pH determination had entirely disappeared in course of the experiments. This quite unanticipated phenomenon prompted him to take in hand a fresh investigation on the machanism of the so-called Kolbe's reaction.

The electrolytes after having been electrolysed for some time were proved to contain certain oxidizing substances, setting iodine free from potassium iodide solution. It is now the author's purpose to determine the amounts of such oxidizing substances formed in course of the electrolyses of the two acetates, and compa e them with those of ethane, which is formed simultaneously.

Experimental.

The apparatus used for electrolysis were the same as those mentioned in the preceding papers, while the conditions under which the electrolyses were carried out, throughout the present investigation, were as follows:

Current density: 10 A/dm^2 excepting the two cases of 0.1% NH_4Ac and 0.1% KAc, where 9 A/dm^2 and 5.1 A/dm^2 were applied respectively.

Temperature: 8–10° C., excepting the cases of electrolytes of the smallest concentrations, where the temp. was raised to 15–20° C.

Test for hydrogen peroxide: The presence of this substance was attested by means of a titanium sulphate solution.

Potassium permanganate test: 20 c.c. of the sample solution was acidified with an excess of sulphuric acid, and titrated by means of n/100 $KMnO_4$ solution.

Potassium iodide and starch test: 20 c.c. of the sample solution was added to KI solution, and iodine set free was titrated with n/100 thiosulphate solution, using a starch solution as the indicator. When reaction is thought to have ceased, a little more KI was added to ascertain its sufficiency.

Table 1.

Electrolyte composition	pH	Duration of electrolysis	After electrolysis pH	H_2O_2	$KMnO_4$	KI+starch	C_2H_6% in the gas sample
NH_4Ac 0.1%	6.65	2½ min.	6.6	abs.	1 drop	no colouration	0
,, 0.3	6.78	6	6.8	trace	1	trace	0
,, 0.5	6.8	10	6.9	,,	3	Thiosulphate 1 drop*	0.1
,, 0.7	,,	14	7.8	pres.	25	11	13.7
,, 1.0	6.9	2	7.5	abs.	3	1	—
,, ,,	,,	20	8.2	pres.	37	1	28.0
,, 3.0	7.0	30	8.3	,,	61	4	28.8
,, ,,	,,	60	,,	,,	255	2	—
,, 5.0	7.05	½	7.1	abs.	2	1	29·3
,, ,,	,,	48	8.2	pres.	130	8	—
,, ,,	,,	96	8.3	,,	750	32	—

* 25 drops = 1 c.c.

From the above table we may gather interesting relations existing between ethane formation and oxidizing action of the electrolysed solutions on potassium iodide. The first two solutions in Table 1 neither evolved ethane, nor gave oxidizing substances (the details of the electrolytic gases were given in the latest paper, loc. cit.). By the 0.5% NH_4Ac solution, which comes third in the table, however, ethane was evolved for the first time, and at the same time some oxidizing substances were found to exist in the solution; like results were obtained in the rest of solutions.

With regard to the 5.0% NH_4Ac solution, the last mentioned in the table, the amount of oxidizing substances was observed gradually to increase as electrolysis went on, while, on the contrary, the quantity of ethane to become less and less. The latter fact was already referred to in the previous paper.

Again, hydrogen peroxide became detectable when electrolysis was continued for some time (in last two cases) but not immediately after its inception (as in the first case). These facts will be more fully stated in the subsequent case of potassium acetate solutions.

The consumption of $KMnO_4$ solution suggests the presence of certain reducing substances. They may be hydrogen peroxide, some other peroxide-

like substances, formaldehyde, or the like. The amount of such reducing substances was also observed to increase with the progress of electrolysis.

The following table shows the results obtained of electrolyses of potassium acetate solutions (0.1%—5.0%).

Table 2

Electrolyte composition	pH	Duration of electrolysis	After electrolysis pH	H_2O_2	$KMnO_4$	KI+starch	C_2H_6% in the gas sample
KAc 0.1%	5.85	2 min.	5.9	abs.	0 drop	No colouration	0
,, 0.4	5.9	6.4	,,	,,	,,	,,	0.2
,, 0.5	,,	8	,,	,,	4	trace	2.8
,, 1.0	,,	15	8.2	pres.	28	Thiosulphate 7 drops	15.2
,, 5.0	6.0	1h. 15m.	8.5	,,	15.5 c.c.	,, 70	27.8

The percentages of ethane evolved from 1.0 and 5.0% potassium acetate solutions were determined by analysing gas samples collected during the first 4 and 3 minutes of electrolysis respectively. In these cases of potassium acetate, the formation of ethane was observed to take place always accompanied with that of oxidizing substances, just as much as in the case of the ammonium salt.

It is also noticeable that when the concentration of the electrolyte was comparatively small, or the pH value of the solution was but slightly raised above 6 no trace of hydrogen peroxide, which seems to have an important bearing on the oxidizing substances in question, was detected. It will, therefore, be highly interesting to push on investigation along this line.

To know how the solutions of potassium acetate behave in course of electrolysis on a broader range of pH, the solutions acidified with acetic acid, or made alkaline by the addition of ammonium carbonate were investigated. The following tables and figures show the results of the electrolysis of a solution, which contained 5.0 gr. KAc and 1.4 gr. HAc per 100 c.c. Although the electrolytic gas in this case was not analyzed, it was approximately estimated by adopting the principle that the electrolytes of similar compositions give similar ethane formation curves, and that the duration of ethane formation is in proportion to the concentration of a like electrolyte, if the current of the same anodic density be applied, the said principle being derived from the results of the experiment No. 4, which treated the (20% KAc+5% HAc) solution, as was described in the first paper and the experiments Nos. 1, 5, 8, 11, 14, 17,

etc. (vid. also the third paper (loc. cit.)) Thus it may be regarded that ethane formation in the above case will reach the maximum point three quarters of an hour after the start of an electrolytic process, and is about

Table 3.

Electrolyte, (KAc 5.0 gr. + HAc 1.4 gr.) per 100 c.c.,
Original pH = 5.0, D_A = 10 A/dm², Temp. = 8—10°C.

Duration of electrolysis	After electrolysis			
	pH	H_2O_2	$KMnO_4$	KI+starch
35 min.	5.5	abs.	4 drops	Thiosulphate 4 drops
45	5.9	,,	,,	5
50	7.3	pres.	20	16
60	7.5	,,	,,	19
70	8.5	,,	2.3 c.c.	17
1½ hours	8.75	,,	6.5	3
2	,,	,,	22	68
2½	8.7	,,	53	9.8 c.c.
3½	,,	,,	110	14.6
4	,,	,,	120	16.4
5	—	,,	160	14.6

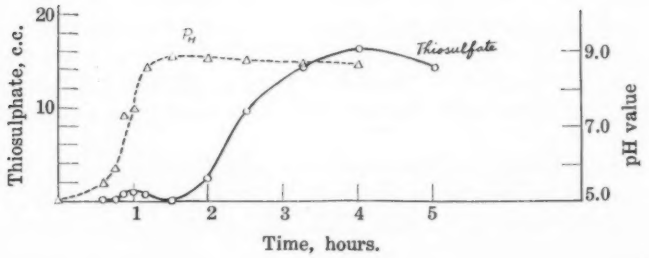

Fig. 1.

(KAc 5.0 gr. / HAc 1.4 gr. per 100 c.c.) solution, D_A=10 A/dm², Temp.=8—10°C.

through in another 45 minutes. These relations lead to the conclusion that ethane formation predominates over the formation of oxidizing substances at the earlier stages of electrolysis, but vice versa at the later stages.

If we assume that acetyl peroxide is first formed at the anode, and the most of it is decomposed at the earlier stages of electrolysis according to the following equation:

$$\underset{\text{acetyl peroxide}}{(CH_3\cdot COO)_2} = \underset{\text{ethane}}{CH_3\cdot CH_3} + 2\,CO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1),$$

and only a small portion of it remains as such, or is decomposed according to the following scheme:

$$\left.\begin{aligned} (CH_3\cdot COO)_2 + H_2O &= CH_3\cdot COOH + \underset{\text{acetic peracid}}{CH_3\cdot COOOH}, \\ CH_3\cdot COOOH + H_2O &= CH_3\cdot COOH + \underset{\text{hydrogen peroxide}}{H_2O_2} \end{aligned}\right\} \ldots\ldots\ldots \quad (2),$$

the decomposition of acetyl peroxide according to the equation (1) must be regarded to decline at the later stages of electrolysis, the chemical change (2) predominating over it. It will be superfluous to say that the two acids involved in the equation (2) take the form of the corresponding salts, when the solution becomes alkaline. This assumption will go a long way to explain the fact, observed so far.

As hydrogen peroxide, which is one of the final decomposition products of acetyl peroxide, easily decomposes in alkaline solutions, its total amount can not continue to increase with the progress of electrolysis, which naturally involves the alkalinity of the solution, but must begin to decrease at a certain point. This explanation will satisfactorily account for why the thiosulphate curve in Fig. 1 falls after once passing over the maximum point. Hydrogen peroxide could not be detected until the electrolysis has been continued for three quarters of an hour, during which the pH of the solution was still below 6.0. Then the pH rose quickly and reached above 7.0 some five minutes later; thereafter hydrogen peroxide was found always present.

The reaction expressed by the second equation of the chemical change (2) is reversible as was pointed out by W.H. Hatcher and G.W. Holden.[1] If so, it is easily conceivable that the formation of hydrogen peroxide according to the second equation is governed by the condition of the electrolyte, in such a manner that an alkaline or a dilute solution favours the formation of hydrogen peroxide, while an acidic or a concentrated one acts contrarily.

The reason, why hydrogen peroxide became detectable after having been absent for the first 45 minutes of electrolysis, can be easily understood, if we take into consideration the pH value of the solution on the one hand

(1) *Trans. Roy. Soc. Canada* [3]**21**, Sect. III. (1927), 237—243: C. 1928, I, 1929.

and the concentration of it on the other. The following table and Fig. 2 relate to the solution of KAc 10.0 gr. and HAc 2.8 gr. per 100 c.c.

Table 4.

Electrolyte, (KAc 10.0 gr. + HAc 2.8 gr.) per 100 c.c.,
Original pH=5.0, D_A=10 A/dm², Temp.=8–10°C.

Duration of electrolysis	After electrolysis			
	pH	H_2O_2	$KMnO_4$	KI+starch
½ hour	5.1	abs.	5 drops	Thiosulphate 2 drops
1½	6.9	,,	10	7
1⅔	7.4	pres.	17	14
2	8.7	,,	2 c.c.	8
3	,,	,,	10	26
4	,,	,,	40	8.6 c.c.
5	,,	,,	110	21.6
6	8.65	,,	105	25.9
8	8.55	,,	150	18.6

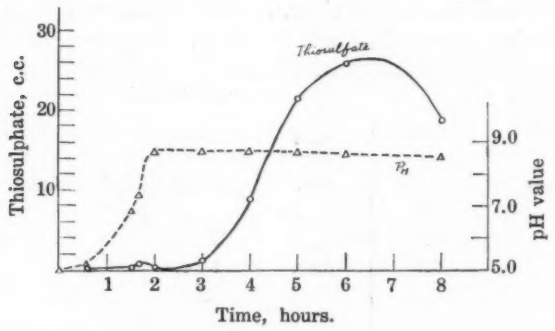

Fig. 2.

$\left(\begin{matrix}\text{KAc 10.0 gr.}\\ \text{HAc 2.8 gr.}\end{matrix}\right.$ per 100 c.c.$\left.\right)$ solution, D_A=10 A/dm², Temp.=8–10°C.

By the same reason as with the previous case it can be assumed that the ethane evolution from the present solution reaches the maximum point somewhere between 1½–2 hours after the commencement of electrolysis; after that it gradually falls until it is nearly done with about an hour later.

Let us now proceed to examine the thiosulphate curve of Fig. 2. After passing a maximum point the curve falls to a minimum point two hours after the start; and then it suddenly leaps up to another maximum point again. The maximum value of thiosulphate consumption is 26.5 c.c. in this case, whereas it was 16.5 c.c. in the preceding one.

It will be readily seen that the maximum point of the ethane formation curve thus coincides with the minimum point of the thiosulphate consumption curve, and the lowest part of the former corresponds with the highest part of the latter. Besides, the maximum value of thiosulphate consumption of the second KAc solution is much higher than that of the first one, although not so high as proportional to the concentration (loc. cit.).

These facts will demonstrate, the author is confident, that ethane has its origin in acetyl peroxide.

Table 5 and Fig. 3 shown below illustrate the results of the electrolysis of the solution containing KAc 20 gr. and HAc 5.6 gr. in 100 c.c. The ethane curve in this figure does not represent this solution but that containing 20% KAc and 5% HAc instead (the first paper, loc. cit.). But the difference between these two solutions being very slight, the curve may be taken as that of the former without significant error.

Table 5.

Electrolyte, (KAc 20.0 gr. + HAc 5.6 gr.) per 100 c.c.,
Original pH = 5.1, D_A = 10 A/dm², Temp. = 8—10°C.

Duration of electrolysis	After electrolysis			
	pH	H_2O_2	$KMnO_4$	KI+starch
¼ hour	5.15	abs.	5 drops	Thiosulphate 1 drop
2½	5.7	,,	—	3
3	7.5	,,	12	9
4	8.7	pres.	2.0 c.c.	5
5	,,	,,	5.5	9
8	8.8	,,	120	12.5 c.c.
10	8.7	,,	145	14.7
13	8.5	,,	220	31.5
16	—	,,	270	18.9

Coincidences between several corresponding points on the ethane and thiosulphate curves can clearly be noticed here. The maximum value of thiosulphate consumption is 31.5 c.c., being greater than those of the fore-

going two solutions. The hours needed for the attainment of these maximum points were nearly proportional to the concentration of the electrolytes; being 4, 6.5 and 13 hours respectively in these three cases.

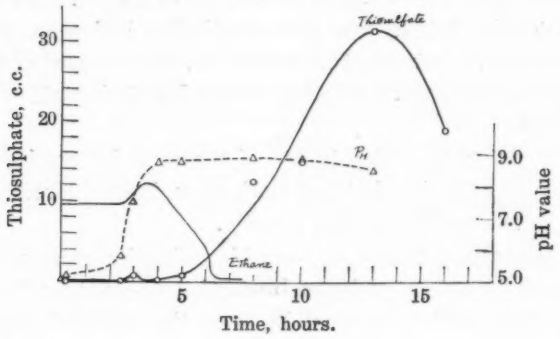

Fig. 3.

$\left(\begin{matrix}\text{KAc } 20.0\text{ gr.} \\ \text{HAc } 5.6\text{ gr.}\end{matrix}\right.$ per 100 c.c.$\Big)$ solution, $D_A = 10$ A/dm², Temp.=8—10°C.

This fact upholds once more, it seems, that acetyl peroxide is one of the principal products of the electrolysis of potassium acetate solutions.

Table 6.

Electrolyte, (KAc 40.0 gr. + HAc 12.0 gr.) per 100 c.c.,
Original pH = 5.1, $D_A = 10$ A/dm², Temp. = 8—10°C.

Duration of electrolysis	After electrolysis			
	pH	H_2O_2	$KMnO_4$	KI+starch
½ hour	5.15	abs.	16 drops	Thiosulphate 4 drops
5½	6.0	,,	37	10
6½	7.3	,,	35	17
8	9.0	,,	32	9
9¾	9.3	,,	15	20

The electrolysis of the (KAc 40 gr. + HAc 12 gr.) per 100 c.c. solution has been traced only so far as 9 hours after the start. The minimum point of thiosulphate consumption lies, at least in this limited range of electrolysis, perhaps at a period of about 8 hours after the start, a fact which can be readily estimated from the foregoing data.

No hydrogen peroxide was detected in this case, even after nearly 10 hours' operation, when the pH value was already as high as 9.3. In the case of the (KAc 20 gr. + HAc 5.6 gr.) per 100 c.c. solution hydrogen peroxide was detected at pH = 8.2, but not at pH = 7.5 yet. In the case of the (KAc 10 gr. + HAc 2.8 gr.) per 100 c.c. solution hydrogen peroxide was detected at pH = 7.4, but not at pH = 6.9 yet. In the case of the (KAc 5.0 gr. + HAc 1.4 gr.) per 100 c.c. solution, it was detected at pH = 7.3, but not at pH = 5.9 yet.

Hydrogen peroxide, which is one of the most interesting compounds, not only from the scientific, but technical, view, is considered so far not to be produced by the anodic reaction directly.

If we assume that hydrogen peroxide makes its appearance according to the equations (2) we can easily understand, by admitting the explanation given above, the relation between its formation and pH value in each of these solutions, and also the fact that the more concentrated are the solutions, the less capable are they of forming H_2O_2 in spite of a comparatively higher value of pH.

The author made an observation in the first paper that a potassium acctatc solution containing ammonium carbonate behaves quite differently from other cases under electrolysis, with extraordinarily small but constant yields of ethane and oxygen throughout the process; the second paper was concerned to somewhat detailed examinations of a similar nature. The following table deals with electrolysis of (KAc 10 gr. + Amm. carbonate 5 gr.) per 100 c.c. solution.

Table 7.

Electrolyte, (KAc 10.0 gr. + Amm. carbonate 5.0 gr.) per 100 c.c.,
Original pH = 8.6, D_A = 10 A/dm², Temp. = 8-10°C.

Duration of electrolysis	After electrolysis			
	pH	H_2O_2	$KMnO_4$	KI+starch
0 hour	8.6	—	—	Thiosulphate 0 drop
1	,,	pres.	35 c.c.	10
$2\frac{1}{2}$	,,	,,	70	1.3 c.c.
5	8.5	,,	250	3.3
7	,,	,,	125	7.5
9	8.1	,,	160	10.4

The comparatively higher value of the original pH of this solution makes us understand that hydrogen peroxide is formed shortly after the start of electrolysis.

Extraordinarily efficient internal oxidation of this solution (vid. the first paper), by corresponding with the very small yields of ethane and oxygen, signifies that a large amount of methyl alcohol is formed there. The more of the $CH_3 \cdot COO$ group of the acetate is changed into the form of methyl alcohol, the less will take the form of ethane or acetyl peroxide, the latter of which may be further transformed into hydrogen peroxide. The comparatively smaller amounts of ethane (vid. the second paper) and thiosulphate consumption in Table 7 both conform to this expectation.

In conclusion of this paper the author begs to express his deepest sense of indebtedness to Professor Dr. M. Matsui of Kyoto Imperial University for his unfailing encouragement and suggestions for the continuation of these studies.

Summary.

(1) The relation between ethane and oxidizing substances in the solutions formed by the electrolyses of acetate solutions is discussed.

(2) It is demonstrated that acetyl peroxide is first formed at the anode, and that ethane is one of its decomposition products.

(3) The presence of hydrogen peroxide in the solutions after electrolysis is attributed to the following hydrolyses of acetyl peroxide:

$$(CH_3 \cdot COO)_2 + H_2O = CH_3 \cdot COOH + CH_3 \cdot COOOH,$$
$$CH_3 \cdot COOOH + H_2O = CH_3 \cdot COOH + H_2O_2.$$

(4) It is discussed how the formation of hydrogen peroxide is related to the pH value of the solution on the one hand and to the concentration of the solution on the other.

(5) The relation existing between the ethane and the hydrogen peroxide formations is also discussed.

(6) It is concluded that the facts observed in the experiments so far carried out by the writer can well be explained by assuming the intermediate formation of acetyl peroxide.

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DAS VERHALTEN DER PYRIDINGRUPPE BEI DER ELEKTROCHEMISCHEN OXYDATION.
I. PYRIDIN.

Von **Moriaki YOKOYAMA** und **Kazuo YAMAMOTO.**

Eingegangen am 22. November, 1931. Ausgegeben am 28. Januar, 1932.

Dass das Pyridin und der Pyridinkern in seinem chemischen Verhalten durch grosse Beständigkeit ausgezeichnet ist, ist allgemein bekannt. Es kann mit konzentrierter Salpetersäure oder Chromsäure gekocht werden ohne Zersetzung zu erleiden[1]; auch von salpetriger Säure wird es nicht verändert[2]. Neuberg[3] erhielt wahrscheinlich Pentose neben viel unverändertem Pyridin mit Wasserstoffsuperoxyd in sauerer Lösung bei Gegenwart von Ferrosulfat. In neuerer Zeit konnten M. Delépine[4] und B.D. Shaw u. A.L. Wilkie[5] Pyridin mit Kaliumpermanganat in sauerer oder alkalischer Lösung zersetzen. J. Dorronsoro[6] erhielt auch Ammoniak und Kohlendioxyd daraus bei Oxydation mit Natriumpersulfat in sauerer Lösung. All diese Forscher kamen aber nur bei erhöhter Temperatur zum Ziele.

Die elektrochemische Oxydation von Pyridin, bezw. des Pyridinkernes ist jedoch bis jetzt nicht untersucht worden. Ferner ist schon oft bei Gelegenheit der Schilderung elektrochemischer Oxydation organischer Verbindungen darauf hingewiesen worden, dass der anodischen Sauerstoff eines der wirksamsten, wenn nicht das wirksamste Oxydationsmittel überhaupt ist. Dah[illegible] interessierte es uns zu studieren, wie das Verhalten von Pyridin, resp. des Pyridinkerns bei Einwirkung von anodischen Sauerstoff ist.

Beschreibung der Versuche.

4 cm³ (3,96 gr.) Pyridin (von Kahlbaum; sp. Gew. 0.981; Sdp. 116°C.) wurden in 150 cm³ 2n. Schwefelsäure gelöst, und in der Tonzelle an einer zylindrischen Bleianode[7] (mit vorher frisch hergestelltem Bleidioxyd-Ueberzug) mit der anodischen Stomdichte von 0.05 Amp/cm² bei 68°C. unter stärker Rührung elektro-oxydiert; die Kathode war ein Platinblech, der Katolyt 2n. Schwefelsäure, und die Strommenge 20F/Mol., welche etwas

(1) Anderson, *Ann.*, **105** (1858), 339.
(2) Oechsner de Coninck, *Bull. Soc. Chem.*, [2], **43** (1885), 180.
(3) *Biochem. Z.*, **184**, (1927), 206.
(4) *Compt. rend.*, **184**, (1927), 206.
(5) *J. Chem. Soc.*, **130** (1928), 1377.
(6) *Chem. Centr.* 1928, II, 1192; *Anales Soc. Espanola Fisica Quim*, **25** (1927), 409.
(7) Bei elektrochemischer Oxydation an Pt-anoden beobachten wir die Entstehung der gleichen Produkten, jedoch in niedrigerer Stromausbeute.

niedriger ist als die theoretische Strommenge bei völligem Abbau nach der Gleichung

$$C_5H_5N+5.5O_2+22F = 5CO_2+NH_3+H_2O.$$

Im Verlauf der Elektrolyse wurde der Anolyt ein wenig bräunlichgelb gefärbt.

A. Die gasförmigen Reaktionsprodukte. Während des Verlaufes der Elektrolyse wurden die in dem Anodenraum entwickelten Gase möglichst sorgfältig analysiert. Denn die dauernde Kontrolle der qualitativen Beschaffenheit der Anodengase während des ganzen Verlaufs der Elektrolyse erschien geeignet, ein klares Bild von der Art und dem Verlauf des Oxydationsprozesses zu vermitteln. Die Gasanalysenmethode wurde nach E. Müller[1] einmal pro Stunde durchgeführt. Wir gebrauchten 3 Hempelsche Pipetten, welche mit den Absorptionsmitteln[2] für Sauerstoff, Kohlendioxyd und Kohlenmonoxyd gefüllt waren.

Einige Analysenresultate aus der grossen Reihe der durchgeführten Versuche wurden in der folgenden Tabelle zusammengestellt. Die Gasvolumina wurde darin auf 0°C. und 760 mm. Druck reduziert. Als Sperrflüssigkeit der Messapparatur diente gesättigte, Kohlendioxyd praktisch nicht absorbierende Natriumchloridlösung[3].

Tabelle 1.

Stromstärke: 2 Amp. Stromdichte: 0.05 Amp./cm². Temperatur: 68°C.

Stunden	Sauerstoffvolumina des O_2-coulometers ccm.	Aufgefangene gasf. Produkte ccm.	Zusammensetung des Anodengases (%)			Verbrauchter Sauerstoff. ccm.	Stromausbeute
			CO_2	CO	O_2		
1	80.7	62.6	22.9	0	77.1	32.4	40.2
2	80.7	68.8	26.6	0	73.4	30.3	37.8
3	80.1	70.8	27.4	0.1	72.5	28.8	36.0
4	80.7	71.0	26.1	0.1	73.8	27.4	34.0
5	80.1	72.3	25.2	0.1	74.7	26.1	32.6
6	80.1	76.9	24.0	0.1	75.1	22.5	28.1
7	80.4	72.7	20.5	0.2	79.3	22.8	29.9
8	78.6	72.2	20.8	0.2	79.0	21.6	27.5
9	81.0	74.4	19.6	0.2	80.2	21.3	26.3
10	80.7	75.0	18.5	0.3	81.2	19.8	24.5
11	80.7	75.4	16.9	0.3	82.8	18.3	22.7
12	80.3	77.2	16.8	0.3	82.9	17.4	21.4
13	81.0	76.6	15.1	0.3	84.6	16.2	20.0

(1) Müller, Elektrochem. Praktikum, 4 Aufl., S., 155.
(2) Yokoyama u. Ishikawa, Dieses Bulletin, **6** (1931), 277.
(3) G. Hoffmann, *Z. angew. Chem.*, **39** (1926), 401.

Tabelle 2.

Stromstärke: 2 Amp. Stromdichte: 0.05 Amp./cm². Temperatur: 20°C.

Stunden	Sauerstoffvolumina des O_2-coulometers ccm.	Aufgefangene gasf. Produkte ccm.	Zusammensetzung des Anodengases (%)			Verbrauchter Sauerstoff. ccm.	Stromausbeute
			CO_2	CO	O_2		
1	80.8	63.9	6.4	0	83.6	27.4	34.0
2	80.6	69.9	7.9	0	92.0	16.5	20.5
3	80.1	71.7	8.4	0.1	91.5	14.6	18.5
4	80.7	74.0	8.4	0.1	91.5	13.1	16.5
5	80.2	75.2	7.8	0.1	92.1	12.4	15.5
6	80.1	76.0	7.6	0.2	92.2	10.8	13.5
7	80.4	76.8	6.4	0.2	93.4	8.6	10.7
8	80.2	77.2	6.1	0.2	93.7	7.8	9.9
9	80.2	77.5	5.9	0.2	93.9	7.5	9.0
10	80.7	77.0	5.5	0.2	94.3	7.4	9.2
11	80.8	78.0	5.1	0.3	94.6	6.9	8.6
12	81.2	78.5	4.8	0.3	94.9	6.8	8.4
13	81.1	79.1	4.7	0.3	95.0	6.0	7.4

Tabelle 3.

Stromstärke: 4 Amp. Stromdichte: 0.1 Amp./cm². Temperatur: 68°C.

Stunden	Sauerstoffvolumina des O_2-coulometers ccm.	Aufgegangene gasf. Produkte ccm.	Zusammensetzung des Anodengases (%)			Verbrauchter Sauerstoff. ccm.	Stromausbeute
			CO_2	CO	O_2		
1	81.6	68.1	20.9	0.1	79.0	25.5	31.3
2	81.6	73.8	23.5	0.1	79.4	25.2	30.8
3	81.6	77.1	20.2	0.2	79.6	21.0	25.7
4	81.6	77.7	19.5	0.2	80.3	19.2	23.5
5	80.7	77.4	13.3	0.3	83.4	16.2	20.1
6	80.1	77.7	13.2	0.3	86.5	12.9	16.1
7	81.0	79.6	11.1	0.3	88.6	11.4	14.1

Tabelle 4.

Stromstärke: 0.4 Amp. Stromdichte: 0.01 Amp./cm².
Temperature: 68°C.

Stunden	Sauerstoff-volumina des O_2-coulometers ccm.	Aufgefangene gasf. Produkte ccm.	Zusammensetzung des Anodengases (%)			Verbrauchter Sauerstoff. ccm.	Stromausbeute
			CO_2	CO	O_2		
1	84.0	40.1	21.7	0	78.3	51.6	61.4
2	80.1	62.1	25.0	0	75.0	38.1	47.5
3	78.9	67.9	31.2	0.1	68.7	33.3	42.1
4	78.9	64.7	30.5	0.1	69.3	32.1	39.3
5	79.5	70.7	26.7	0.2	73.1	27.9	35.0
6	79.2	69.8	25.8	0.2	74.0	26.4	33.3
7	79.8	71.3	24.4	0.2	75.2	26.7	32.7
8	79.5	70.7	23.3	0.2	76.5	25.5	32.1
9	79.5	69.5	22.0	0.2	77.8	25.5	32.1
10	80.1	72.3	21.2	0.2	78.6	25.5	31.9
14	81.0	70.8	20.5	0.2	79.3	24.0	30.0
20	79.8	67.4	15.6	0.2	84.2	22.1	28.9
40	81.9	72.5	14.1	0.2	85.7	19.8	24.2

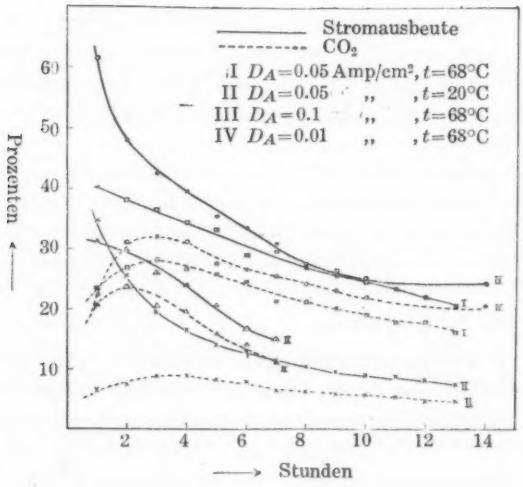


Fig. 1.

Wie aus der Tabelle (1)–(4) und den Kurven (Fig. 1) ersichtlich ist, sind Kohlendioxyd und wenig Kohlenmonoxyd im Anodengase enthalten, das Verhalten des Anodengases je nach der Elektrolysebedingungen unterschiedlich und die am Anfang erwähnten Bedingungen die besserer, sodass wir auch bei den meisten Versuchen diese Bedingungen einhalten.

B. Die in Aether leicht löslichen Produkte. Nach der Elektrolyse wurde der Anolyt zunächst mit Aether mehrmals ausgeschüttelt. Die Aetherlösung hinterliess nach dem Abdestillieren des Aethers eine stechend nach Ameisensäure riehende, etwas gelb gefärbte Flüssigkeit, die gegen Lackmus sauer reagierte, aus Mercurichlorid Mercurochlorid abschied und Permanganatlösung entfärbte. Sie wurde mit Bariumcarbonatbrei neutralisiert und filtriert um überschüssiges Bariumcarbonat zu entfernen. Nach Verdampfen des Filtrats erhielten wir Bariumformiat. (Ausbeute: etwa 0.05 gr. pro Versuch).

Das Bariumsalz, das im Verlauf von 10 Einzelversuchen aufgesammelt wurde, nach dem Reinigen mit Tierkohle und Umkrystallisieren im Vakuum über Schwefelsäure bis zur Gewichtkonstanz getrocknet und analysiert.

0.1553 gr. gaben nach Abrauchen mit Schwefelsäure 0.1589 gr. $BaSO_4$. Gef. Ba=60.20%
Ber. für $(CHO_2)_2$ Ba : Ba=60.42%

C. Die mit Wasserdampf nicht flüchtigen Produkte. Die mit Aether extrahierte Lösung des Anolyten wurde zuerst mit Bariumhydroxydlösung und am Ende mit Bariumcarbonat vorsichtig neutralisiert und dadurch von Schwefelsäure vollständig befreit. Die so erhaltene filtrierte Lösung wurde im Wasserdampfstrom langsam, bis das Destillat gegen Nessler'sches Reagenz nicht mehr reagierte, destilliert, wobei der Aufnahmekolben etwa 100 ccm Wasser enthielt und mit Eis von aussen gekühlt wurde um flüchtige Gase leicht aufzufangen.

Der etwa gelbegefärbte Rückstand der Wasserdampfdestillation wurde im Vakuum zur Trockne eindampft. Er hinterliess ein hellgelb gefärbtes krystallinisches Produkt. Aus seiner wässrigen Lösung wurde nach Filtrieren und Reinigen mit Tierkohle schöne weisse prismatische Nadeln erhalten, die durch die typischen Reaktionen als Bariumnitrat identifiziert wurden. (Ausbeute: 0.5 gr.).

D. Die mit Wasserdampf flüchtigen Produkte. Das Destillat der Wasserdampfdestillation, das gegen Lackmus schwach alkalisch reagierte, wurde mit Salzsäure neutralisiert und dann im Vakuum bis zur vollständigen Trockne zur Befreiung von Pyridinhydrochlorid eingedampft. Wir erhielten dabei eine kleine Menge einer weissen krystallinischen Masse, die hygroskopisch war.

Sie wurde mit wenig Wasser aufgenommen, auf dem Wasserbad verdampft und hinterliess weisse nadelförmige krystalle, die mit absolutem Alkohol in einen unlöslichen Teil (a) und einen leicht löslichen Teil (b) zerlegt werden konnten.

(*a*) *Die in Alkohol unlösliche Substanz.* In der in Alkohol nicht löslichen Substanz konnte leicht Ammoniak nachgewiesen werden mit Hilfe der bekannten Geruchsprobe nach Zusatz von Kalilauge. Wir stellten nach dem Umkrystallisieren aus Wasser das Platinchloriddoppelsalz dar, dessen Analyse folgende Werte ergab.

0.1377 gr. Platindoppelsalz ergaben nach dem Glühen 0.0604 gr. Platin. Gef. Pt=43.86% Ber. für $(NH_4)_2PtCl_6$: Pt=43.96%

Ausbeute: 0.15 gr.

(*b*) *Die in Alkohol leicht löslichen Substanzen.* Die Alkohollösung hinterliess nach dem Verdampfen des Alkohols weisse Nadelkrystalle, die chlorhaltig und etwas hygroscopisch waren und bei 210°–237°C. schmolzen unter gleichzeitigem Sublimieren. Der fischartige Geruch nach dem Zusatz von Kalilauge liess auf Methylamin und seine Verwandten schliessen. Nach dem Umkrystallisieren aus Alkohol und Trocknen über Schwefelsäure im Vakuum wurde die krystalline Masse der Analyse unterworfen.

0.0971, 0.1455 gr. Subst. gaben mit $AgNO_3$ 0.1809, 0.2715 gr. AgCl. Gef. Cl = 46.78, 46.16%.

Berechnet sich für Methylaminchlorid 52.52%Cl; für Dimethylaminchlorid 43.49%Cl; für Trimethylaminchlorid 37.11%Cl.

Diesen Beobachtungen nach handelt es sich vemutlich um eine Mischung der Hydrochloride von Methylamin und seine Verwandten.

Wie lässt sich aber die Bildung von Methylamin und seiner Verwandten erklären? Sie scheint zunächst schwer verstandlich, aber mir Hilfe folgender Ueberlegung könnte man sich die Bildung vorstellen. Wir nehmen an, dass durch den Angriff der Pyridinmolekel gleichzeitig Formaldehyd und Ammoniak, resp. Ammoniumsulfat entstehen. Die Stromwärme an der Anode veranlasst nun die Kondensation der beiden Substanzen nach J. Plöchl[1] nach folgenden Gleichungen

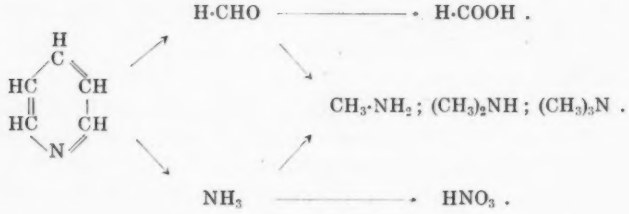
$$(NH_4)_2SO_4 + 3CH_2O \rightarrow (CH_3NH_2)_2 \cdot H_2SO_4 + CO_2$$
$$(CH_3NH_2) \cdot H_2SO_4 + 3CH_2O \rightarrow [(CH_3)_2NH]_2 \cdot H_2SO_4 + CO_2$$
$$[(CH_3)_2NH] \cdot H_2SO_4 + 3CH_2O \rightarrow [(CH_3)_3N]_2 \cdot H_2SO_4 + CO_2,$$

sodass in dem Anolyt ein Gemisch von Mono-, Di-, und Trimethylamin entsteht.

(1) *Ber.*, **21** (1888), 2117; vgl. H. Emde u. Hornemann, *Helv. Chim. Acta.*, **14** (1931), 892.

Wir hatten eine Mischung von Formaldehyd und Ammoniumsulfatlösung in einem Blindversuche elektro-oxydiert und in der Tat eine ähnliches Basengemisch darstellen können, wie wir es bei der elektrochemischen Oxydation von Pyridin erhalten hatten.

Unter Zusammenfassung aller Beobachungen lässt sich einstweilen folgendes vorläufige Schema über den Oxydationsverlauf am Pyridinkern aufstellen wobei die letzten Stufen Kohlenmonoxyd und Kohlendioxyd noch nicht berücksichtigt sind); es lautet:



Zusammenfassung.

(1) Das gegen Hitze sowie gegen starke Oxydationsmittel sehr wiederstandfähige Pyridin wurde in seinem Verhalten gegen anodischen Sauerstoff untersucht.

(2) Bei der elektrochemischen Oxydation des Pyridins an der Bleidioxydanode in verdünnter Schwefelsäure erhält man die folgenden Oxydationsprodukte: Kohlendioxyd, Kohlenmonoxyd, Salptersäure, Ameisensäure, Ammoniak und Formaldehyd, welch letzteres durch sofortige Kondensation mit Ammoniak Methylamin und seine Verwandten ergibt.

(3) Während der Analyse wurde der kinetische Verlauf der Gasabscheidung an der Anode unter verschiedenen Elektrolysebedingungen analytisch verfolgt.

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